PRODUCTION OF BIODIESEL FROM CASTOR OIL USING EGG SHELL WASTE AS SOLID CATALYSTS

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ABSTRACT

The increase in price of petroleum and environmental concerns, the search for alternative fuels has gained importance. Biodiesel is one of several alternative fuels that is renewable and can be manufactured from vegetable oils. Biodiesel's physical properties are similar to those of petroleum diesel, but it is a cleaner-burning alternative. Using biodiesel in place of petroleum diesel can reduce emissions. The main objectives of the research is to produce biodiesel from castor oil using activated egg shell waste as solid catalysts and to investigate the effect of methanol/oil ratio, temperature and reaction time on the biodiesel yield. The effect of parameters on the biodiesel yield has been investigated from the reaction process that is called transterification process. Biodiesel has been successfully produced from castor oil using activated egg shell waste as solid catalyst by the variation of methanol/oil ratio, temperature and reaction time has affected the biodiesel yield. The highest biodiesel yield was found by the methanol/oil ratio of 5:1, temperature of 55°C and reaction time of 4 hours.

ABSTRAK

Disebabkan oleh kenaikan harga minyak mentah dan kebimbangan terhadap alam sekitar, penyelidikan terhapda bahan bakar alternatif telah menjadi lebih penting. Biodiesel adalah salah satu daripada beberapa bahan bakar alternatif yang boleh diperbaharui dan boleh diperbuat daripada minyak sayuran. Sifat fizikal biodiesel adalah sama dengan minyak mentah, tetapi ia adalah alternatif pembakaran yang lebih bersih. Menggunakan biodiesel di tempat minyak mentah boleh mengurangkan pencemaran udara. Objektif utama penyelidikan ini adalah untuk menghasilkan biodiesel daripada minyak kastor menggunakan sisa cangkerang telur yang diaktifkan sebagai pemangkin dan untuk mengkaji kesan nisbah metanol / minyak, suhu dan masa reaksi pada hasil biodiesel. Kesan parameter pada hasil biodiesel diperoleh dari proses tindak balas yang dipanggil proses transester. Biodiesel telah berjaya dihasilkan daripada minyak kastor menggunakan sisa cangkerang telur diaktifkan sebagai pemangkin pepejal oleh variasi nisbah metanol/minyak, suhu dan masa tindak balas telah dapat menghasilkan biodiesel. Hasil biodiesel tertinggi didapati oleh nisbah metanol/minyak pada 5:1, suhu pada 55°C dan reaksi masa selama 4 jam.

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LIST OF SYMBOLS

%	Percent
°C	Degree Celsius
°F	Degree Ferinheight
g	Gram
h	Hour
mL	Milliliter
µL	Microliter
µm	Micrometer
Wt %	Weight percent

LIST OF ABBREVIATIONS

BaO	Barium Oxide
$CaCO_3$	Calcium Carbonate
CaO	Calcium Oxide
FAME	Fatty acid methyl esters
GC-MS	Gas chromatography–mass spectrometry
H_2SO_4	Sulphuric Acid
HCl	Hydrochloric Acid
K_2CO_3	Potassium Carbonate
KOH	Potassium Hydroxide
MeOH	Methanol
MgO	Magnesium Oxide
Na_2CO_3	Sodium Carbonate
NaOH	Sodium Hydroxide
SrO	Strontium Oxide
ZnO	Zinc Oxide

CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

Recent concerns over the environment, increasing fuel prices, and scarcity of supply have promoted interest in the development of alternative source to petroleum fuels. Due to the global prices of fuel are going up day after day, biodiesel extracted from vegetable oil is one such renewable alternative under consideration. The production of biodiesel would be cheap as it could be extracted from non-edible oil sources. Biodiesel has been defined as a mono-alkyl ester of vegetable oil or animal fats (Knothe, 2005). These resources can be re-grown and considered infinite in comparison to crude oil that is limited. When using biodiesel instead of petrodiesel, the demand for crude oil products is reduced and as a result their prices decrease. There are many types of vegetable oil such as castor oil, jatropha oil, and soybean oil. Biodiesel is produced through a refinery process called transesterification reaction of vegetable oils and animal fat. This process is a reaction of the oil with an alcohol to remove the glycerin, which is a by-product of biodiesel production.

Many researchers use edible oils such as soybean oil and corn oil to produce biodiesel. The price of edible oils keeps increasing due to demand for nutritional need. In order to overcome this issue, castor oil is the best option to make biodiesel because it is easier to plant and costs less than soybean, sunflower or other seeds. Castor oil is a triglyceride of various fatty acids and about 10% glycerine. The fatty acids consist of approximately 80–90% ricinoleic acid, 3–6% linoleic acid, 2–4% oleic acid and 1–5% saturated fatty acids (Pazir and Muhammad, 1991).

The production processes for biodiesel are well known. There are three basic routes to biodiesel production from oils and fats that is: (a) Base catalyzed transesterification of the oil, (b) Direct acid catalyzed transesterification of the oil, and (c) Conversion of the oil to its fatty acids and then to biodiesel. Most of the biodiesel produced today is done with the base catalyzed reaction because it is low temperature and pressure; it yields high conversion (98%) with minimal side reactions and reaction time (Anonymous, 2007).

Different studies have been carried out using different alcohol. Among the alcohols that can be used in the transesterification reaction are methanol, ethanol, propanol, butanol and amyl alcohol. Methanol and ethanol are used most frequently. Ethanol is a preferred alcohol in the transesterification process compared to methanol because it is derived from agricultural products and is renewable and biologically less objectionable in the environment, however methanol is the most commonly used alcohol because of its low cost and its physical and chemical advantages associated with being polar and the shortest chain alcohol. The reaction time is shorter in the methanolysis because of the physical and chemical properties of methanol. The production of castor oil was faster with methanol compared with ethanol (Meneghetti, 2006).

The conventional production of biodiesel proceeds in transesterification of oils or fats using homogeneous catalysts but it will cause production of wastewater from washing process of catalyst residues and unreusability of the catalysts (Macleod et. al., 2008). Therefore, the development of heterogeneous solid catalyst has recently gained much attention on view of separation and does not produce soap through free fatty acid neutralization and triglyceride saponification. Generally, $Ca(NO_3)_2$ or $Ca(OH)_2$ is the raw material to produce CaO. There are several natural calcium sources from wastes such as egg shell, mollusk shell, and bone. Solid catalyst is not dissolved in the reaction and it can easily separate from products. The catalyst can be regenerated and reused and it is environmental friendly.

This research is about the production of biodiesel from castor oil using egg shell waste as solid catalyst in batch system.

1.2 PROBLEM STATEMENT

The world demands for diesel keep increasing year by year. We have to face the fact that the world going to run out of oil eventually. Diesel from fossil oil are limited and non renewable. Feasibility of raw material for diesel product is looking forward. Therefore, this research will be focus on the optimum parameter and catalyst to improved yield and quality of biodiesel fuel.

1.3 RESEARCH OBJECTIVES

The objective of this experiment is to produce biodiesel from castor oil using activated egg shell waste as solid catalysts and to investigate the effect of methanol/oil ratio, temperature and reaction time on the biodiesel yield

1.4 SCOPES OF STUDY

In order to achieve the objective of this research, the scope of study has been determined:

1. Preparation of activated egg shell as solid catalyst.
2. Transesterification of castor oil with activated egg shell to produce biodiesel.
3. Investigation the temperature, reaction time, methanol/oil ratio effect on the biodiesel yield
4. Analyze the biodiesel yield using Gas Chromatography and ASTM standards.

1.5 SIGNIFICANCE OF STUDY

Petroleum content in the world today is significantly reduced and need an alternative fuel to cover the market demand. Therefore, biodiesel production has been seen as an alternative fuel. For production of biodiesel, the choice of feedstock depends largely on the resources availability. The most assessed vegetable oils in the transesterification reaction are the castor, corn, cottonseed, crambe, peanut, soybean, palm, rapeseed, and sunflower oils, mainly due to their content of glycerides (Demirbas, 2005). Castor bean is one of the raw materials that are available in Malaysia and the oil can be extract to produce biodiesel since castor oil is amongst the plants with the highest oil yield potential. Several heterogeneous catalyst have been employed in the biodiesel production but using egg shell as a catalyst is a new development to convert waste to wealth. Wei et al. (2009) have done their studies from soybean oil that is edible oil but due to demand for nutritional need, feedstock from non edible oil has been looking forward.

CHAPTER 2

LITERATURE REVIEW

2.1 BIODIESEL

The history of biodiesel starts in the mid 1800's. In those days the process of transesterfication was used to separate glycerine from oil. Rudolf Diesel (1858-1913) developed the first engine to run on peanut oil. When Rudolf Diesel demonstrated his diesel engine at the Paris Show in 1900, he ran it on straight peanut oil.

Technically, biodiesel is defined as mono-alkyl esters of long chain fatty acids derived from renewable feed stocks like vegetable oils or animal fats which conform to ASTM D6751 specifications (EN 14214 in Europe) for use in diesel engines. It is biodegradable, non-toxic, show low emission profiles and also is beneficial environmentally (Fangrui and Milford, 1999). The biodiesel fuels derived from oils or fats with significant amounts of saturated fatty compounds will display higher cloud points and pour points (Bhale et al., 2008).

Non-edible vegetable oils, such as Pongamia pinnata (Karanja or Honge), Jatropha curcas (Jatropha or Ratanjyote), Madhuca iondica (Mahua) and Castor Oil have also been found to be suitable for biodiesel production (Yusuf et al., 2011). There are four primary techniques for biodiesel production: direct use and blending of raw oils, micro emulsions, thermal cracking and transesterification (Siddiquee and Rohani, 2011). Alkyl esters can be produced through transesterification of triglycerides, which are separated by immiscibility and higher density (Marchetti et al., 2007).

Transesterification (also called alcoholysis) is the reaction of a fat or oil with an alcohol (with or without catalyst) to form esters and glycerol. Since the reaction is reversible, excess alcohol is used to shift the equilibrium to the product side (Fangrui and Milford, 1999). Under transesterification reaction with alcohol the first step is the conversion of triglycerides to diglycerides, which is followed by the subsequent conversion of higher glycerides to lower glycerides and then to glycerol, yielding one methyl ester molecule from each glyceride at each step (Hideki et al., 2001).

Biodiesel production is a very modern and technological area for researchers due to the relevance that it is winning everyday because of the increase in the petroleum price and the environmental advantages (Mustafa, 2011). It is an alternatives fuel for diesel engines that is produced by chemical reaction of a vegetable oils or animal fats with an alcohol such as methanol. The product is called as methyl ester or biodiesel, which is receiving high attention as an alternative, nontoxic, biodegradable and renewable diesel fuels (Ma and Hanna, 1999). When biodiesel displaces petroleum diesel, it reduces global warming gas emission such as carbon dioxide. Biodiesel has no aromatics, almost no sulfur and contains 11% oxygen by weight. These characteristics of biodiesel reduces the emissions of carbon monoxide, hydrocarbon and particulate matter in the exhaust gas compare petroleum-based diesel fuels (Graboski and McCormick, 1998). Therefore, biodiesel has become one of the most common bio-fuels in the world (Lin et al., 2011).

2.2 RAW MATERIAL

There are several types of raw materials for biodiesel production. The most common feedstock comes from vegetable oil. There are two types of vegetable oils that are edible and non-edible oils. More than 95% of biodiesel production feedstocks come from edible oils since they are mainly produced in many regions and the properties of biodiesel produced from these oils are much suitable to be used as diesel fuel substitute. By converting edible oils into biodiesel, food resources are actually being converted into automotive fuels. It is believed that large-scale production of biodiesel from edible

oils may bring global imbalance to the food supply and demand market (Gui et al., 2008).

2.2.1 Edible Oil

2.2.1.1 Soybean Oil

Soybean oil is one of the major feedstocks for biodiesel production. Soybean oil has five fatty acids: approximately equal amounts of palmitic acid, oleic acid, and linolenic acid (about 13% each), linoleic acid (approximately 55%), and stearic acid (approximately 4%) (Kinney and Clemente, 2005).

2.2.2 Non-Edible Oil

2.2.2.1 Jatropha Oil

Jatropha oil is produced from the seeds of jatropha that has the capacity to grow in marginal and common lands. Jatropha contain high seed yield and high oil content (Wood, 2005). Jatropha oil can be used as renewable source like biodiesel.

2.2.2.2 Castor Oil

Castor oil is one of the top ten oils in the world and needs only 4 months for harvesting. Considering all the options available among non-edible vegetable oil, *riccinnus communis* has been identified as the most suitable seed. Castor oil (*riccinnus communis*) is the best source for creating biodiesel (Anonymous, 2001). Castor oil and its derivatives, besides being used in medicine, are used in a wide range of sectors including agriculture, textile industry, paper industry, high quality lubricants, plastics engineering, rubber and pharmaceuticals (Ogunniyi, 2006). Consequently, there has been a steady increase in the demand of castor oil and its products in the world market due to their renewable nature, biodegradability and eco-friendliness. The use of castor oil as biodiesel has proven to have technical and ecological benefits and provides opportunities for agricultural development in marginal and sub-marginal lands.

2.3 CATALYST

A substance that speeds up a chemical reaction, but is not consumed by the reaction; hence the catalyst can be recovered unchanged at the end of the reaction. Excess amount of catalyst would lead to the higher amount of production cost and reduce product yield (Ma and Hanna, 1999). Catalyst used in the transesterification of triglycerides can be classified as homogeneous, heterogeneous and enzyme catalyst.

2.3.1 Homogeneous Catalyst

Homogeneous catalysts function in the same phase (liquid, gaseous, etc.) as the reactants. Homogeneous catalysts are dissolved in a solvent with the substrates. Basically, in this transesterification process, there are two types of homogeneous catalyst which is acid catalyst (H_2SO_4 or HCl) and alkali catalyst (KOH or NaOH). Homogeneous basic catalyst provides much faster reaction rates than heterogeneous catalyst, but it is difficult to separate homogeneous catalyst from the reaction mixture (Du *et al.*, 2004).

2.3.2 Heterogeneous Catalyst

Heterogeneous catalysis occurs in a different phase than the reactants. Heterogeneous catalysts are more economical and ecologically friendly. Heterogeneous catalysts are also easier to separate from liquid products and can be designed to give higher activity, selectivity and longer lifetimes (Tanabe and Holderich, 1999). Because of these advantages, research on chemical reaction using solid bases as catalysts has increased over the past decade. The use of heterogeneous catalysts does not produce soap through free fatty acid neutralization and triglyceride saponification. The most commonly studies for heterogeneous basic catalysts are alkaline metals carbonates (Na_2CO_3, K_2CO_3), alkaline earth metal carbonates ($CaCO_3$), alkaline earth metal oxides (CaO, MgO, SrO, BaO) and other oxides as ZnO (Verziu et al., 2008).

2.4 TRANSESTERIFICATION PROCESS

In the transesterification of different types of oils, triglycerides react with an alcohol, generally methanol or ethanol, to produce esters and glycerin. To make it possible, a catalyst is added to the reaction.

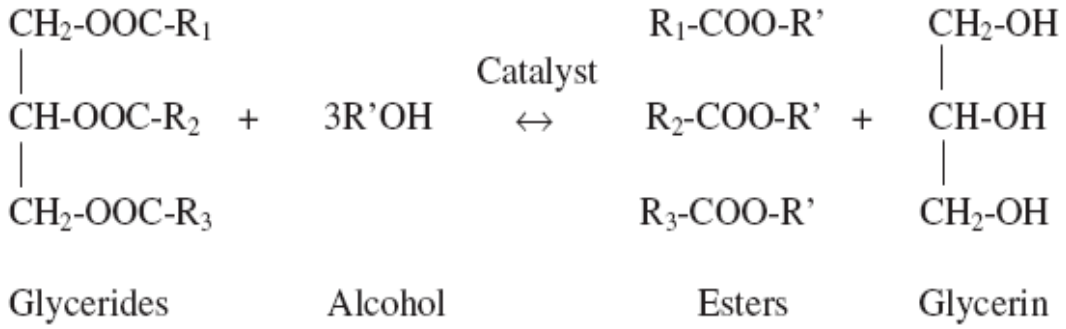


Figure 2.1: Reaction for oil transesterification

Transesterification or alcoholysis is the displacement of alcohol from an ester by another in a process similar to hydrolysis, except than alcohol is used instead of water (Srivatava and Prasad, 2000). This process has been widely used to reduce the high viscosity of triglycerides. The transesterification reaction is represented by the general equation as in the following equation. Transesterification is one of the reversible reactions and proceeds essentially by mixing the reactants. However, the presence of a catalyst (a strong acid or base) will accelerate the conversion.

Transesterification of triglycerides with methanol and aid of catalyst produce methyl ester and glycerol. The glycerol layer settles down at the bottom of the reaction vessel. The step wise reactions are reversible and a little excess of alcohol is used to shift the equilibrium towards the formation of esters. In presence of excess alcohol, the forward reaction is first order reaction and the reverse reaction is found to be second order reaction. Alkaline-catalyzed transesterifications proceed considerably faster than acid–catalyzed transesterifications (Freedman et al., 1984).

CHAPTER 3

METHODOLOGY

There will be an explanation about the material used and detailed procedure that be going through in the experiment to achieve the objective of this research.

3.1 MATERIALS

3.1.1 Chemical

3.1.1.1 Castor Oil

The raw material that is castor oil was bought from Sigma-Aldrich. The structure of the major component of castor oil are Ricinoleic acid, a monounsaturated, 18-carbon fatty acid, is unusual in that it has a hydroxyl functional group on the twelfth carbon. This functional group causes ricinoleic acid (and castor oil) to be unusually polar, and also allows chemical derivatization that is not practical with most other seed oils. It is the hydroxyl group which makes castor oil and ricinoleic acid valuable as chemical feed stocks.

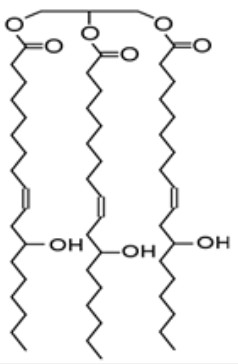
Average composition of Castor seed oil / fatty acid chains				Structure of the major component of castor oil
Acid name	Average Percentage Range			
Ricinoleic acid	85	to	95%	
Oleic acid	6	to	2%	
Linoleic acid	5	to	1%	
Linolenic acid	1	to	0.5%	
Stearic acid	1	to	0.5%	
Palmitic acid	1	to	0.5%	
Dihydroxystearic acid	0.5	to	0.3%	
Others	0.5	to	0.2%	

Figure 3.1: Average composition of fatty acid chain and structure of the major component of castor oil.

Source: http://casakinabalu.com,2012

Table 3.1: Properties of Castor oil

Colour	Failtly Yellow
Relative Density at 20°C	0.952-0.965
Moisture	0.3% max.
Iodine Value	82-90
Acid Value	2.0 max.
Peroxide Value	5.0 max.

3.1.1.2 Solid Catalyst

Solid catalyst used in this research is made from waste egg shell. We explored the possibility of application of egg shell as a catalyst in catalytic process in biodiesel production. The chemical composition (by weight) of eggshell has been reported as follows: Calcium carbonate (94%), Magnesium carbonate (1%), Calcium phosphate (1 %), and Organic matter (4%) (Stadelman, 2000).

3.1.1.3 Methanol

Methanol is the simplest alcohol also known as methyl alcohol, wood alcohol, wood naphtha or wood spirits. It is light, volatile, colorless, flammable chemical with formula CH_3OH (often abbreviated MeOH). At room temperature it is a polar liquid. Boiling point for methanol is at 64.96°C (148.93°F) and solidifies at -93.9°C (-137°F).

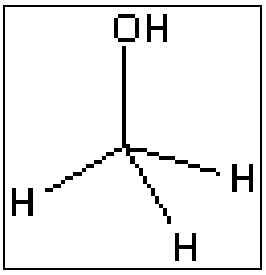


Figure 3.2: Formula structure of methanol

3.1.2 Apparatus

The list of major apparatus that used in this research

i. Two neck round bottom flask, 1000 mL
ii. Reflux condenser
iii. Separator funel
iv. Thermometer
v. Beaker
vi. Retot stand

3.1.3 Equipments

The list of major equipment used in this research

i. Weight balance
ii. Magnetic stirrer with hot plate
iii. Rotaty evaporator
iv. Gas chromatography

3.1.3.1 Rotary Evaporator Working Principle

Rotary evaporator is used to evaporate solvents under vacuum condition with the use of heat and rotation. The rotation of the evaporation flask is to distribute the surface into bigger surface to increase the evaporation process. As the flask is rotationg, heat is applied by immersed the flask in a water bath. Rotation leads to more efficient temperature transfer. The function of vacuum is to lower the boiling temperature thus minimizing damage to thermolabile substances.

Figure 3.3: Rotary Evaporator

3.1.3.2 Gas Chromatography Working Principle

Gas chromatograph (GC) is one of the common types of chromatography in analytical chemistry for separating and analysis. Figure 3.4 show gas chromatography principle. Usually GC is used to detect the compound that can be vaporized without decomposition. The mobile phase is a carrier gas, usually an inert gas such as helium or an unreactive gas such as nitrogen.

In all chromatographic separations the sample is transported in a mobile phase, which may be a gas, a liquid, or a supercritical fluid. This mobile phase is then forced through an immiscible stationary phase, which is fixed in place in a column or on a solid surface. The two phases are chosen so that the components of the sample distribute themselves between the mobile and stationary phase to varying degrees.

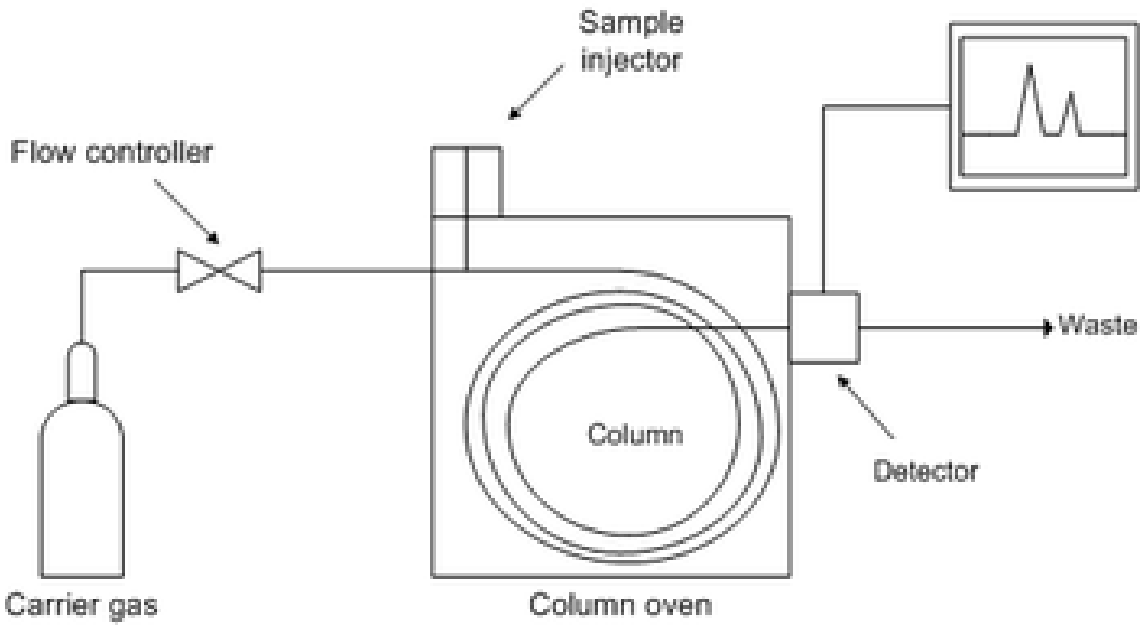


Figure 3.4: Gas chromatography principle